Main-Chain Motions of a Liquid Crystalline Cellulose Derivative as Revealed by Dielectric Measurements

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COMMUNICATION

Main-Chain Motions of a Liquid Crystalline Cellulose Derivative as Revealed by Dielectric Measurements

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Dielectric relaxation processes of polysaccharides and their derivatives have been the subject of many reports[1]. Dielectric measurements in those studies, however, were limited mostly to temperatures below the glass transition T_g, where only local side-chain motions were observed. Measurements at higher temperatures become increasingly difficult due to often destructive contributions to conductance from ionic impurities, which are difficult to remove perfectly.

Cellulose is an unmeltable semi-rigid polymer, whose T_g and melting temperature can be dramatically lowered by introducing an appropriate side chain, most effectively, in a chemically disordered fashion. Such cellulose derivatives often form a thermotropic liquid crystal (LC)[2]. Fully cyanoethylated 2,3-dihydroxypropyl cellulose (CN-DHPC) is a chemically disordered LC polymer which is characterized by low T_g and an extraordinarily high dielectric constant[3]. Extensive purification of this polymer has allowed us to make dielectric measurements up to a remarkably high temperature. This communication reports the first observation of two dielectric relaxations above T_g for this polymer, the first observation among polysaccharide systems and among semi-rigid, thermotropic LC polymers.

The molecular and physical characteristics of a CN-DHPC sample, coded DH-4-CN, are listed in Table 1. It has T_g at −28°C and forms a LC phase between

Table 1. Molecular and Physical Characteristics of Sample DH-4-CN.

$10^{-4} \cdot Mn$[a]	MS[b]	T_g	T_{sa}[c]	T_{ai}[d]
4.5	4	−28°C	17°C	90°C

a) Number-average molecular weight estimated by GPC.
b) Molar substitution of di-hydroxypropyl unit.
c) Rubbery solid-to-anisotropic liquid transition temperature.
d) Anisotropic-to-isotropic transition temperature.

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17°C and 90°C. Dielectric measurements were made on a Hewlett-Packerd precision LCR meter Model 4284A, in a temperature range between 150 K and 350 K and a frequency range between 20 Hz and 1 MHz. A three-terminal dielectric cell specially designed for fluid LC polymers was employed. Temeprature was measured with a copper vs. constantan thermocouple along with a Keithley 196 system DMM. Experimental details including sample preparation and characterization will be reported elsewhere[3].

Figure 1 shows the temperature dependence of dielectric constant ε' and dielectric loss ε'' measured at three representative frequencies 50 Hz, 500 Hz and 5 kHz. The loss factor curve for each frequency clearly shows three relaxations, which we shall denote β, α and α' in the increasing order of temperature. For each relaxation, the temperature at which ε'' is maximum increases with increasing frequency f. The plot of ε'' against frequency and of ε'' against ε' (figures not shown) were resolved into three relaxation components at a fixed temperature. In Figure 2, the logarithm of f_{max} is plotted against T^{-1}, where f_{max} is the relaxation frequency. These Arrhenius plots give activation energies of 55 kJ/mol, 143 kJ/mol and 73 kJ/mol for the β, α and α' relaxations, respectively.

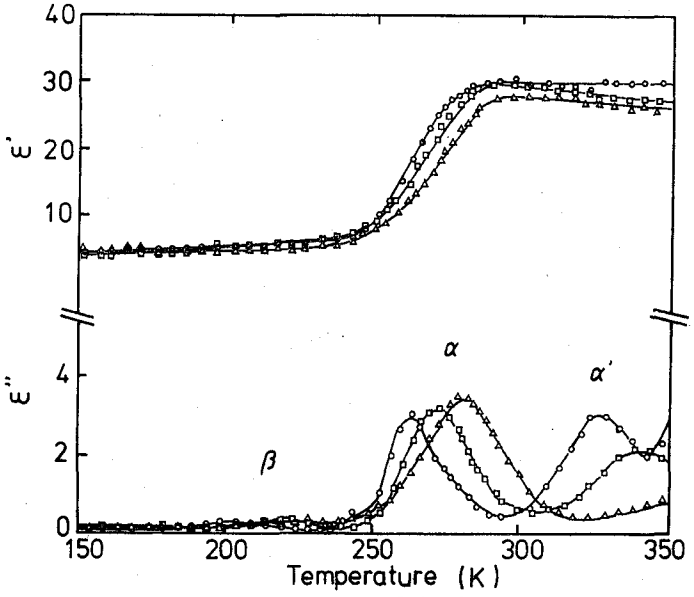

Fig. 1. Temperature dependence of (top) dielectric constant ε' and (bottom) dielectric loss ε'' for DH-4-CN at 50 Hz (○), 500 Hz (□) and 5 kHz (△).

The β relaxation, which is mainly observed below T_g, may be assigned to the local mode of side chain motions. The temperature range as well as the activation energy of this mode agree with those reported for cyanoethyl cellulose and assigned likewise[1d].

Striking is the fact that the present polymer exhibits two relaxations above T_g. The α relaxation, which becomes observable at temperatures about 10°C or more

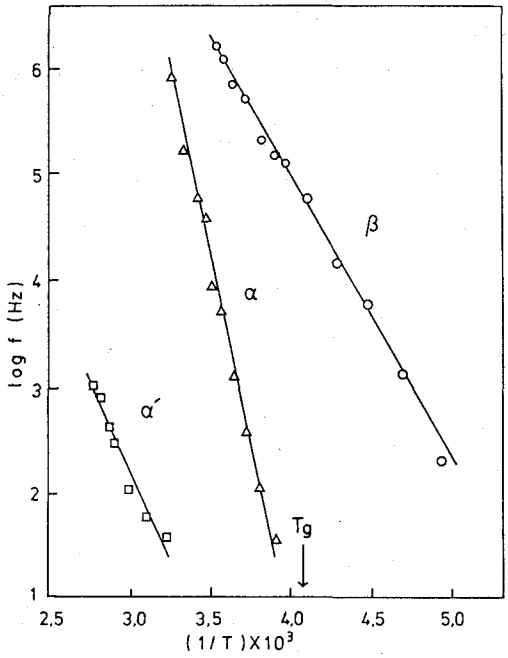

Fig. 2. Arrhenius plots of frequency at maximum f_{max} of dielectric loss ε'' for DH-4-CN.

above T_g may be reasonably assigned to a micro-Brownian motion of the main chain. In fact, the Arrhenius plot extrapolated to a small value of f_{max} indicates a close correlation of this relaxation with T_g. The α' relaxation is observed at higher temperatures than the α mode, its activation energy being about half that of the latter. This means that the two relaxations are relevant to main-chain motions of different modes. The Arrhenius plot in this case indicates a correlation of the α' mode with the temperature T_{sa} above which the system shows obvious fluidity and anisotropy. Because the α relaxation is observable even at temperatures higher than the isotropization temperature T_{ai}, this mode is unlikely to be related to the liquid crystalline order of the molecules. Perhaps, the α' mode is related to a main-chain motion of a relatively large scale, larger than that of the α mode, that is possible only when the system becomes fluid enough. The rigidity or semi-rigidity of the chain may have something to do with the existence of the two relaxation processes above T_g. An X-ray analysis shows no indication of crystallinity in the temperature region between T_g and T_{sa}. A more extensive study is in progress.

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